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(52) INDOLENEINE DERIVATIVES.

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(55) Indolenine derivatives represented by general formula (I), wherein R¹ represents a hydrogen atom or a lower alkyl group, and X and Y may be the same or different from each other and each represents a methylene group or an oxygen atom are disclosed. They are useful compounds as intermediates for synthesizing cyanine compounds to be favorably used as organic near-infrared absorbing dyes for use in an optical disc recording medium using a semiconductor laser.

SPECIFICATION

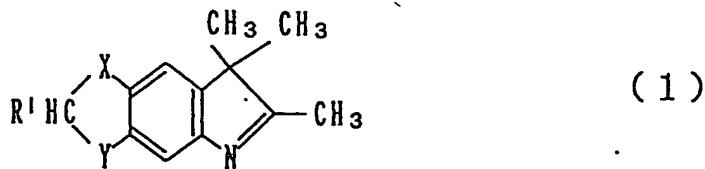
INDOLENINE DERIVATIVE

FIELD OF THE INVENTION

The present invention relates to novel indolenine derivatives.

DISCLOSURE OF THE INVENTION

The indolenine derivative of the present invention is a compound undisclosed in literature and is represented by the formula (1)

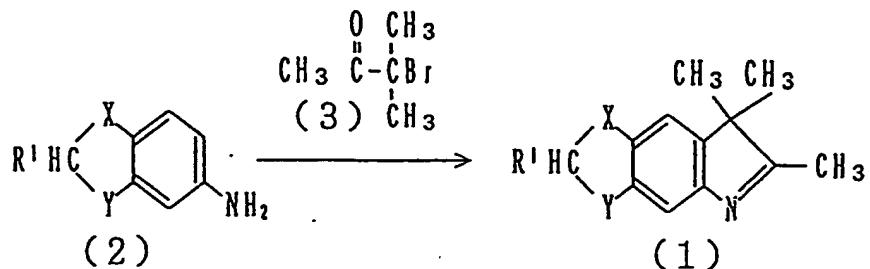


wherein R^1 is a hydrogen atom or a lower alkyl group, X and Y are the same or different and each represent a methylene group or an oxygen atom.

The compounds of the present invention represented by the formula (1) are useful as an intermediate for synthesizing the cyanine compounds represented by the formula (8) which appear hereinafter.

The compounds of the present invention can be prepared by various processes, and can be easily prepared, for example, by the following preferable process.

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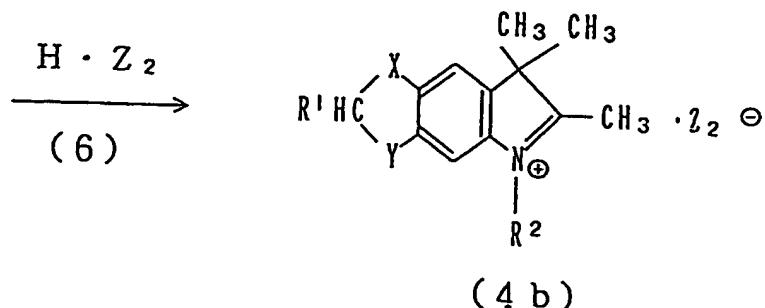
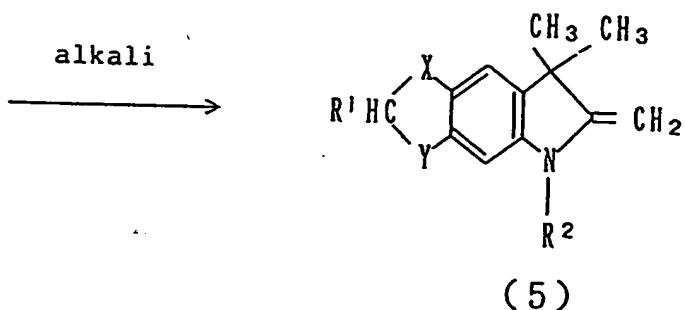
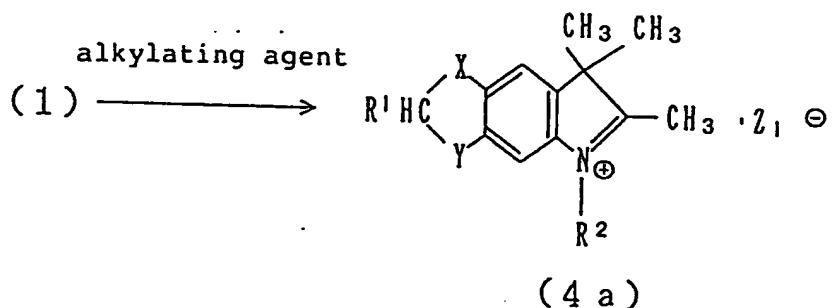
The conventional aniline derivative of the formula (2) is reacted with the conventional 3-bromo-3-methyl-2-butanone of the formula (3) in the presence of an acid scavenger. Useful acid scavengers are, for example, pyridine, triethylamine, tri-n-propylamine, tri-n-butylamine and like tertiary amines; sodium carbonate, potassium carbonate, calcium carbonate and like alkali metal salts of carbonic acids; sodium acetate, potassium acetate, calcium acetate and like alkali metal salts of acetic acids; etc. The acid scavenger is used in an amount of usually about 0.3 to about 5 moles, preferably about 0.5 to about 1.5 moles, per mole of the compound of the formula (2). The proportions of the compounds of the formulas (2) and (3) are usually about 0.3 to about 5 moles, preferably about 0.5 to about 1.5 moles, of the latter per mole of the former. The reaction is conducted usually at a temperature in the range of from ambient temperature to about 200°C, preferably about 50 to about 150°C and is completed usually in several hours to about

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25 hours, preferably about 5 to about 15 hours.

The compound of the present invention thus obtained can be readily isolated from the reaction mixture and purified by commonly employed separation and purification means such as recrystallization, column chromatography or the like.

The compound of the present invention can be made into the cyanine compound of the formula (8) by the following process:



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In the above formulas, R¹, X and Y are as defined above, Z₁ is an acidic residue other than perchlorate residue and tetrafluoroborate residue, Z₂ is a perchlorate residue or a tetrafluoroborate residue, and R² is an optionally substituted lower alkyl group.

The compound represented by the formula (4a) can be prepared by causing an alkylating agent to act on the indolenine derivative of the formula (1). Examples of the alkylating agent are methyl toluenesulfonate, ethyl toluenesulfonate, n-propyl toluenesulfonate, isopropyl toluenesulfonate, n-butyl toluenesulfonate and like alkyl toluenesulfonates, ethyl bromide, n-propyl bromide, n-butyl bromide, ethyl iodide, n-propyl iodide, n-propyl chloride, n-butyl chloride and like halogenated alkyls, dimethyl sulfate, diethyl sulfate and like dialkyl sulfates, a mixture of acids and epoxy compounds (for example, a mixture of hydrochloric acid, sulfuric acid or like inorganic acid, acetic acid, propionic acid or like organic acid and ethylene oxide, propylene oxide or the like), methyl sultone, ethyl sultone, propyl sultone, butyl sultone and like alkyl sultones, etc. The amount of the alkylating agent to be used is usually about 0.3 to about 5 moles, preferably about 0.5 to about 2 moles, per mole of the compound of the formula (1). The reaction is carried out in the presence or the absence of a solvent.

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Illustrative of useful solvents are toluene, xylene and like alkylbenzenes; n-octane, n-decane, cyclohexane, decalin and like aliphatic hydrocarbons; benzene, naphthalin, tetralin and like aromatic hydrocarbons; trichloroethane, tetrachloroethane, chlorobenzene, dichlorobenzene and like halogenated hydrocarbons, etc. The reaction is effected usually at a temperature in the range of from room temperature to about 200°C, preferably about 50 to about 150°C, and is completed in usually about 2 to about 30 hours, preferably about 5 to about 25 hours.

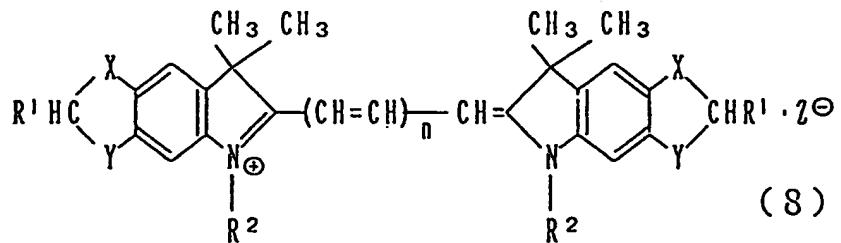
The compound of the formula (5) can be prepared by treating the compound of the formula (4a) with alkali in a suitable solvent such as water. Useful alkalis can be any of those heretofore used, such as sodium hydroxide, potassium hydroxide and the like. The alkali is used in an amount of about 1 to about 20 moles, preferably about 1 to about 5 moles, per mole of the compound of the formula (4a). The amount of the solvent to be used is usually about 2 to about 100 mlies, preferably about 2 to about 20 moles, per mole of the compound of the formula (4a). The reaction is performed usually at 0 to about 150°C, preferably 0 to about 100°C, and is completed usually in tens of minutes to about 10 hours, preferably about 1 to about 5 hours.

The compound of the formula (4b) can be produced

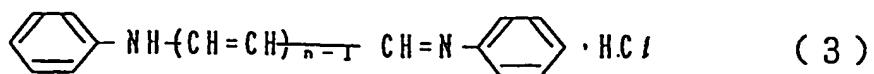
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by reacting the compound of the formula (5) with the compound of the formula (6) in an appropriate solvent such as methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butanol, isobutyl alcohol, tert-butyl alcohol and like alcohols; benzene, toluene, xylene, n-octane, n-decane, cyclohexane, decalin, trichloroethane, tetrachloroethane, chlorobenzene, dichlorobenzene and like hydrocarbons, etc. The proportions of the compounds of the formulas (5) and (6) are about 0.3 to about 10 moles, preferably about 0.5 to about 3 moles, of the latter per mole of the former. The reaction is conducted at 0 to about 70°C and is usually completed in about 10 minutes to about 3 hours.

The cyanine compounds represented by the formula



wherein R¹, R², X and Y are as defined above, Z is an acidic residue, and n is 2 or 3, can be prepared by subjecting to condensation reaction the indolenium salt (the compounds of the formulas (4a) and (4b)) obtained above and a known compound represented by the formula



wherein n is as defined above.

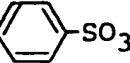
Shown below are specific examples of the groups represented by R¹, R² and Z in the formula (8).

Examples of the lower alkyl group are methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-hexyl, n-heptyl, n-octyl and like C₁-C₈ alkyl groups.

Examples of the substituents for the lower alkyl group are C₁-C₈ alkoxy, hydroxyl, sulfonic acid group, carboxy, (C₁-C₈ alkyl)amino, phenylsulfonyl amino, p-methylphenylsulfonyl amino, acetoxy, (C₁-C₃ alkoxy)carbonyl, (C₁-C₃ alkoxy)(C₁-C₃ alkoxy)carbonyl and the like. Specific examples of the lower alkyl group having such substituents are methoxymethyl, ethoxymethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-(n-butoxy)ethyl, n-butoxymethyl, 2-hydroxyethyl, a group -(CH₂)_m-SO₃N_a (wherein m is an integer of 1 to 8), methylaminomethyl, dimethylaminomethyl, 2-(p-methylphenylsulfonylamino)ethyl, acetoxyethyl, methoxycarbonylmethyl, methoxymethoxy-methyl, 2-ethoxyethoxyethyl, etc.

Examples of the group Z are halogen atom, alkyl sulfonate residue, arylsulfonate residue, perchlorate residue, tetrafluoroborate residue, arylcarboxylic acid residue and the like. When Z is a halogen atom, examples of Z⁻ are Cl⁻, Br⁻, I⁻, F⁻ and the like. When Z is an alkyl sulfate residue, examples of Z⁻ are CH₃SO₄⁻,

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$C_2H_5SO_4^-$, $n-C_3H_7SO_4^-$, $n-C_4H_9SO_4^-$ and the like. When Z is an arylsulfonate residue, examples of Z^- are - SO_3^- , $CH_3-\text{C}_6\text{H}_4-\text{SO}_3^-$ and the like. When Z is a perchlorate residue, examples of Z^- include ClO_4^- and the like. When Z is a tetrafluoroborate residue, examples of Z^- include BF_4^- and the like. When Z is an arylcarboxylic acid residue, examples of Z^- are - COO^- and the like.

The foregoing condensation reaction is conducted in an anhydrous organic solvent in the presence of a fatty acid salt. Useful fatty acid salts are, for example, sodium acetate, potassium acetate, calcium acetate, sodium propionate, potassium propionate and the like. The fatty acid salt is used usually in an amount of about 0.5 to about 3 moles, preferably about 1 to about 2 moles, per mole of the compound of the formula (4a) or (4b).

Examples of the anhydrous organic acid are acetic anhydride, propionic anhydride, butyric anhydride, γ -butyrolactone and the like. Such anhydrous organic acid is used usually in an amount of about 10 to about 100 moles, preferably about 20 to about 50 moles, per mole of the compound of the formula (4a) or (4b). The proportions of the compound of the formula (4a) or (4b) and the compound of the formula (7) are about 0.2 to about 1.5 moles, preferably about 0.4 to about 0.7 mole, of the latter per mole of the former. The reaction smoothly

proceeds at a temperature of about 50 to about 150°C, preferably about 70 to about 140°C, and is usually completed in about 10 to about 60 minutes.

The compound prepared by any of the foregoing processes can be isolated from the reaction mixture and purified with ease by usual separation and purification means such as recrystallization, column chromatography or the like.

The cyanine compounds of the formula (8) obtained above are useful for the following applications. More specifically, the cyanine compounds of the formula (8) has a good solubility in an organic solvent such as methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butanol, isobutanol, tert-butanol, diacetone alcohol or like alcohol, dichloromethane, dichloroethane or like aliphatic halogenated hydrocarbons, or the like. The compounds of the invention have a maximum absorption at 670 to 830 nm and has a high molar absorptivity coefficient. When used as an optical disc recording medium adapted for semiconductor laser recording, the compounds exhibit an outstanding optical reflectivity on exposure to the laser beam for reproduction, hence especially valuable for use. Further, the compounds of the formula (8) which are capable of achieving a marked absorption as compared with usual dyes are suitable for

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use as a dye for filters, or as a photosensitive material or a sensitizing dye for photosensitive materials in copying and printing. Moreover, the compounds are usable as an agent for medical diagnosis for examining the function of livers, as a dye for Langmuir-Blodgett film, etc.

In addition, the compounds of the invention are useful as intermediates for production of functional dyes such as photochromic materials or the like.

EXAMPLES

Given below are Examples illustrating the preparation of the compounds of the present invention and Reference Examples illustrating the preparation of the compounds of the formula (8).

Example 1

A mixture of 20.57 g of 3,4-methylenedioxy-aniline, 24.76 g of 3-bromo-3-methyl-2-butanone and 75 ml of pyridine was reacted at a temperature of 50 to 55°C for 5 hours and further reacted with refluxing for 10 hours. After completion of the reaction, the reaction mixture was added to 100 ml of water and the solution was extracted with 50 ml of dichloromethane. After removal of the solvent, the residue was subjected to vacuum distillation, giving 11.64 g of 2,3,3-trimethyl-5,6-methylenedioxyindolenine.

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Boiling point: 134 to 136°C/4 to 5 mmHg

Elemental analysis	C	H	N
Found (%)	70.6	6.5	6.7
Calcd. (%)	70.92	6.45	6.89

Example 2

A mixture of 20.00 g of 5-aminoindane, 27.23 g of 3-bromo-3-methyl-2-butanone and 60 ml of pyridine was treated in the same manner as in Example 1, giving 17.60 g of the compound of the formula (1) (wherein R¹=H, X=methylene, Y=methylene).

Boiling point: 122 to 130°C/3 to 4 mmHg

Elemental analysis	C	H	N
Found (%)	84.3	8.7	6.9
Calcd. (%)	84.37	8.60	7.03

Example 3

The same procedure as in Example 1 was repeated using 19.76 g of the compound of the formula (2) (wherein R¹=methyl, X=O, Y=methylene), giving 11.72 g of the compound of the formula (1) (wherein R¹=methyl, X=O, Y=methylene).

Boiling point: 139 to 145°C/5 to 6 mmHg

Elemental analysis	C	H	N
Found (%)	77.9	8.1	6.4
Calcd. (%)	78.10	7.96	6.51

Example 4

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A 11.65 g quantity of the compound of the formula (1) (wherein R¹=methyl, X=methylene, Y=O) was prepared in the same manner as in Example 1 using 19.76 g of the compound of the formula (2) (wherein R¹=methyl, X=methylene, Y=O).

Boiling point: 130 to 135°C/3 to 4 mmHg

Elemental analysis	C	H	N
Found (%)	77.8	8.1	6.3
Calcd. (%)	78.10	7.96	6.51

Reference Example 1

A mixture of 10.16 g of 2,3,3-trimethyl-5,6-methylenedioxyindolenine obtained above in Example 1, 13.67 g of n-butyl p-toluenesulfonate and 40 ml of chlorobenzene was reacted with refluxing for 20 hours. After completion of the reaction, 1-(n-butyl)-2,3,3-trimethyl-5,6-methylenedioxyindolenium·toluenesulfonate was extracted with 60 ml of water.

To the extract was added 20 g of 20% NaOH and the mixture was reacted at 70°C for 3 hours, followed by extraction with 30 ml of toluene. After the toluene was distilled off, the residue was subjected to vacuum distillation, giving 5.25 g of 1-(n-butyl)-3,3-dimethyl-2-methylene-5,6-methylenedioxyindoline.

Boling point: 162 to 164°C/5 to 6 mmHg

A 3.24 g quantity of 70% HClO₄ was added to a

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mixture of 5.00 g of 1-(n-butyl)-3,3-dimethyl-2-methylen-5,6-methylenedioxyindoline obtained above and 100 ml of isopropyl alcohol at a temperature of up to 20°C. The mixture obtained was stirred at room temperature for 1 hour and cooled to not higher than 5°C. The precipitated crystals were separated by filtration, washed and dried, giving 6.94 g of 1-(n-butyl)-2,3,3-trimethyl-5,6-methylenedioxyindolenium-perchlorate.

Melting point: 147.0 to 150.0°C

To 20 ml of acetic anhydride were added 1.45 g of 1-(n-butyl)-2,3,3-trimethyl-5,6-methylenedioxy-indolenium-perchlorate, 0.52 g of 8-anilino-acrolein-anile hydrochloride and 0.68 g of potassium acetate. The resulting mixture was refluxed for 10 minutes and poured into 100 ml of water. The precipitated crystals were separated by filtration, washed with water and recrystallized from methanol, giving 1.05 g of the compound of the formula (8) (wherein R¹=H, R²=n-butyl, X=O, Y=O, Z⁻=ClO₄⁻, n=2). Given below are the melting point, wavelength at maximum absorption (λ_{max}) and molar absorptivity coefficient (ϵ) of the obtained compound.

Melting point: 242.0 to 243.0°C

λ_{max} : 696 nm (methanol)

ϵ : $1.76 \times 10^5 \text{ cm}^{-1} \cdot \text{M}^{-1}$

Reference Example 2

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A 5.20 g quantity of the compound of the formula (8) (wherein R¹=H, R²=ethyl, X=O, Y=O, Z⁻=I⁻, n=2) was prepared in the same manner as in Reference Example 1 using 10.15 g of the compound of the formula (1) (wherein R¹=H, X=O, Y=O).

The wavelength at maximum absorption (λ_{\max}) of the obtained compound was 694 nm (methanol).

Reference Example 3

The same procedure as in Reference Example 1 was repeated using 15.00 g of the compound of the formula (1) (wherein R¹=H, X=O, Y=O), giving 6.00 g of the compound of the formula (8) (wherein R¹=H, R²=2-methoxyethyl, X=O, Y=O, Z⁻=ClO₄⁻, n=3).

The obtained compound had a wavelength of 793 nm (methanol) at maximum absorption (λ_{\max}).

Reference Example 4

A 2.09 g quantity of the compound of the formula (8) (wherein R¹=methyl, R²=n-butyl, X=O, Y=methylene, Z⁻=ClO₄⁻, n=2) was prepared in the same manner as in Reference Example 1 using 6.45 g of the compound of the formula (1) (wherein R¹=methyl, X=O, Y=methylene). Given below are the melting point, wavelength at maximum absorption (λ_{\max}) and molar absorptivity coefficient (ϵ) of the thus obtained compound.

Melting point: 227 to 228°C

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λ_{max} : 695 nm (diacetone alcohol)

ϵ : $1.94 \times 10^5 \text{ cm}^{-1}$

Reference Example 5

The same procedure as in Reference Example 1 was repeated using 6.45 g of the compound of the formula (1) (wherein R¹=methyl, X=methylene, Y=O), giving 2.76 g of the compound of the formula (8) (wherein R¹=methyl, R²=n-butyl, X=methylene, Y=O, Z⁻=ClO₄⁻, n=2). The compound had a melting point, wavelength at maximum absorption (λ_{max}) and molar absorptivity coefficient (ϵ) as shown below:

Melting point: 215 to 217°C

λ_{max} : 688 nm (diacetone alcohol)

ϵ : $1.90 \times 10^5 \text{ cm}^{-1}$

Reference Example 6

A 2.20 g quantity of the compound of the formula (8) (wherein R¹=H, R²=n-butyl, X=methylene, Y=methylene, Z⁻=ClO₄⁻, n=2) was obtained by conducting the same procedure as in Reference Example 1 using 4.00 g of the compound of the formula (1) (wherein R¹=H, X=methylene, Y=methylene). Given below are the melting point, wavelength at maximum absorption (λ_{max}) and molar absorptivity coefficient (ϵ) of the obtained compound.

Melting point: 163 to 165°C

λ_{max} : 670 nm (diacetone alcohol)

ϵ : $2.24 \times 10^5 \text{ cm}^{-1}$

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Reference Example 7

The compound of the formula (8) (wherein R¹=H, R²=2-ethoxyethyl, X=methylene, Y=methylene, Z⁻=ClO₄⁻, n=2) was prepared in the same manner as in Reference Example 1 using the compound of the formula (1) (wherein R¹=H, X=methylene, Y=methylene). The compound thus obtained had a wavelength at maximum absorption (λ_{max}) and molar absorptivity coefficient (ϵ) as shown below.

λ_{max} : 672 nm (diacetone alcohol)

ϵ : 2.20×10^5 cm⁻¹

Reference Example 8

The same procedure as in Reference Example 1 was repeated using the compound of the formula (1) (wherein R¹=H, X=methylene, Y=methylene), giving the compound of the formula (8) (wherein R¹=H, R²=2-acetoxyethyl, X=methylene, Y=methylene, Z⁻=BF₄⁻, n=3). The wavelength at maximum absorption (λ_{max}) and molar absorptivity coefficient (ϵ) of the obtained compound were as follows.

λ_{max} : 768 nm

ϵ : 2.28×10^5 cm⁻¹

Reference Example 9

The compound of the formula (8) (wherein R¹=H, R²=2-methoxyethyl, X=methylene, Y=methylene, Z⁻=I⁻, n=3) was obtained in the same manner as in Reference Example 1 using the compound of the formula (1) (wherein R¹=H,

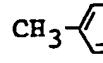
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X=methylene, Y=methylene). Given below are the wavelength at maximum absorption (λ_{max}) and molar absorptivity coefficient (ϵ) of the obtained compound.

λ_{max} : 768 nm

ϵ : $2.30 \times 10^5 \text{ cm}^{-1}$

Reference Example 10

The same procedure as in Reference Example 1 was repeated using the compound of the formula (1) (wherein R¹=H, X=O, Y=O), giving the compound of the formula (8) (wherein R¹=H, R²=2-hydroxyethyl, X=O, Y=O, Z⁻=CH₃--SO₃⁻, n=2). The obtained compound had a wavelength at maximum absorption (λ_{max}) and molar absorptivity coefficient (ϵ) as given below.

λ_{max} : 695 nm (diacetone alcohol)

ϵ : $1.70 \times 10^5 \text{ cm}^{-1}$

Reference Example 11

The compound of the formula (8) (wherein R¹=H, R²=-C₂H₄SO₃Na, X=O, Y=O, Z⁻=Cl⁻, n=3) was obtained in the same manner as in Reference Example 1 using the compound of the formula (1) (wherein R¹=H, X=O, Y=O). Given below are the wavelength at maximum absorption (λ_{max}) and molar absorptivity coefficient (ϵ) of the obtained compound.

λ_{max} : 790 nm (methanol)

ϵ : $1.60 \times 10^5 \text{ cm}^{-1}$

Reference Example 12

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The same procedure as in Reference Example 1 was repeated using the compound of the formula (1) (wherein R¹=methyl, X=O, Y=methylene), giving the compound of the formula (8) (wherein R¹=methyl, R²=n-butyl, X=O, Y=methylene, Z⁻=C₂H₅SO₄⁻, n=3). The compound had a wavelength at maximum absorption (λ_{max}) and molar absorptivity coefficient (ϵ) as shown below.

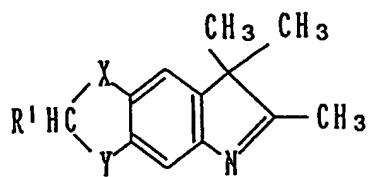
λ_{max} : 795 nm (methanol)

ϵ : 1.93 $\times 10^5$ cm⁻¹

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CLAIMS:

1. An indolenine derivative represented by the formula



wherein R^1 is a hydrogen atom or a lower alkyl group, X and Y are the same or different and each represent a methylene group or an oxygen atom.

2. A compound according to claim 1 wherein X and Y are both a methylene group.

3. A compound according to claim 1 wherein X and Y are both an oxygen atom.

4. A compound according to claim 1 wherein X is a methylene group and Y is an oxygen atom.

5. A compound according to claim 1 wherein X is an oxygen atom and Y is a methylene group.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP89/00944

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl⁴ C07D209/70, C07D491/048, C07D491/056

II. FIELDS SEARCHED

Minimum Documentation Searched :

Classification System	Classification Symbols
IPC	C07D209/70, C07D491/048, C07D491/056
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *	

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	JP, A, 63-66186 (Tokuyama Soda Co., Ltd.) 24 March 1988 (24. 03. 88) (Family: none)	1 - 5

* Special categories of cited documents: ¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"S" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

October 4, 1989 (04. 10. 89)

Date of Mailing of this International Search Report

October 23, 1989 (23. 10. 89)

International Searching Authority

Japanese Patent Office

Signature of Authorized Officer